

III.A.8 Functionally Graded Cathodes for Solid-Oxide Fuel Cells

Objectives

- Elucidate the mechanism of the oxygen-reduction reaction using *in situ* vibrational spectroscopy and *ab initio* analysis.
- Develop micro-impedance spectroscopy system to discern the reaction mechanisms for oxygen reduction and to elucidate the effect of electrode geometry on overall performance of SOFCs.
- Complete the construction of an ultra high vacuum (UHV) system for temperature programmed desorption (TPD) and sticking probability measurements relevant to O₂-cathode interactions.
- Analyze the kinetics of oxygen-reduction reactions occurring at charged mixed ionic-electronic conductors (MIECs) using two-dimensional finite volume models with *ab initio* calculations.
- Determine oxygen permeation rate through dense silver membranes to estimate the oxygen transport rate under SOFC operating conditions.

Accomplishments

- Two distinct oxygen bands appeared at 825 and 1131 cm⁻¹, corresponding to peroxo- and superoxo-like species, respectively, when partially reduced CeO₂ was exposed to 10% O₂. Periodic density functional theory (DFT) calculations aided the interpretation of spectroscopic observations.
- A lanthanum strontium manganese (LSM) microelectrode (ME) generated from a patterned LSM electrode was used to examine the electrode-geometry effect using micro-impedance spectroscopy.
- A UHV system has been built for fundamental study of cathode materials under well-controlled conditions.

Meilin Liu (Primary Contact), Harry Abernathy, SongHo Choi, Y. M. Choi, Charles Compson, Jian Dong, Erik Koep, David Mebane, Robert Williams, Jr.

Georgia Institute of Technology
School of Materials Science and Engineering
771 Ferst Drive, Atlanta, GA 30332-0245
Phone: (404) 894-6114; Fax: (404) 894-9140
E-mail: meilin.liu@mse.gatech.edu

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336;
E-mail: Lane.Wilson@netl.doe.gov

- A numerical finite volume scheme was devised to solve a nonlinear DC polarization problem for mixed conductor thin films in two dimensions, including the effect of sheet resistance.
- Oxygen permeation through dense silver membranes was determined to follow an Arrhenius relation with an activation energy of 0.94 eV (21.7 kcal mol⁻¹). The effective leaking current density was calculated to be 0.0146 mA cm⁻² at 750°C.

Introduction

This project has centered on elucidating the reaction mechanism of oxygen reduction on SOFC cathode materials using experimental measurements in conjunction with advanced theoretical tools (i.e., quantum-chemical calculations and continuum modeling). Accelerating the oxygen-reduction rate is imperative to reduce the cathode/electrolyte interfacial polarization resistance, which can be achieved by understanding the elementary steps of the oxygen-reduction reaction. The elementary steps of oxygen reduction on cathode materials generally include: (1) molecular and dissociative adsorption of oxygen species, (2) dissociation of adsorbed oxygen species along with charge transfer, (3) diffusion of adsorbed molecular or dissociated oxygen species to the cathode/electrolyte interface, and (4) incorporation of partially charged oxygen ions into the electrolyte lattice.

Approach

Experimental methods along with theoretical analyses have been carried out to guide the design of functionally graded cathode materials in SOFCs. *In situ* vibrational spectroscopy in conjunction with advanced *ab initio* surface modeling was applied to measure surface oxygen species at various metal-oxide surfaces. Micro-impedance spectroscopy has been utilized to elucidate the reaction mechanism of oxygen reduction and to better discern the effect of electrode geometry on the cathode materials. A TPD system has been set-up to study adsorbed oxygen species on cathode materials while concurrently running *in situ* vibrational spectroscopy. To examine the surface mechanism of LSM thin films, we have produced a model of direct current (DC) response in thin films. The inert properties of silver over a wide temperature range could prove it a strong candidate for intermediate-temperature SOFC interconnect applications. Therefore, the oxygen permeation rate through dense silver was measured in

order to determine the effective leaking current density under SOFC operating conditions.

Results

Interactions between O_2 and CeO_2 were examined experimentally by *in situ* Raman spectroscopy and theoretically by density functional slab model calculations. The ceria studies were carried out as a way to test our quantum-chemical calculation methods since the structure of ceria is simpler than the mixed conducting oxide perovskites used for SOFC cathodes. As illustrated in Figure 1(a), when partially reduced CeO_2 was exposed to 10% O_2 , two distinct oxygen bands appeared at 825 and 1131 cm^{-1} , corresponding to peroxy- and superoxy-like species, respectively. In order to verify the peaks were indeed an oxygen-containing species, another Raman spectrum was recorded by exposing the sample to 10% $^{18}O_2$ and observing any shift in peak position. Periodic DFT calculations based on the surface mode shown in Figure 1(b) aided the interpretation of spectroscopic observations and provided energetics and geometrical information for the dioxygen species adsorbed on CeO_2 . The O_2 adsorption energies on unreduced CeO_2 surfaces are endothermic ($0.91 < \Delta E_{ads} < 0.98$ eV), while those on reduced surfaces are exothermic ($-4.0 < \Delta E_{ads} < -0.9$ eV), depending on other relevant surface processes such as chemisorption and diffusion into the bulk. Partial reduction of surface Ce^{4+} to Ce^{3+} (together with the formation of oxygen vacancies) can alter geometrical parameters and, accordingly, lead to a shift in the vibrational frequencies of adsorbed oxygen species compared to those on unreduced CeO_2 . Moreover, the location of oxygen vacancies affects the formation and subsequent dissociation of oxygen species on the surfaces. DFT predictions of the adsorption energetics support the

experimental observation that oxygen adsorption and reduction is energetically more favorable on reduced ceria surfaces than on unreduced surfaces.

To examine adsorbed oxygen species on cathode materials, nanoparticles of the desired mixed oxides (LSM, lanthanum strontium cobalt [LSC], and samarium strontium cobalt [SSC]) were deposited on a yttria-stabilized zirconia (YSZ) substrate using combustion CVD (CCVD). To generate a surface enhanced Raman signal (SERS) effect, silver nanoparticles were deposited simultaneously with the cathode material. Besides having a greater intensity, the SERS spectrum also has more distinct peaks. The key to observing adsorbed oxygen peaks in the Raman spectra – besides having a high exposed surface area – is having a surface sufficiently clear of surface hydroxyl groups and other unwanted adsorbants before exposing the sample to oxygen. We are currently testing various evacuation regimens at different temperatures to find a method that cleans the cathode surface sufficiently enough to generate a detectable adsorbed oxygen species signal.

Shown in Figures 2(a) and 2(b) are typical SEM images of a tungsten carbide (WC) tip used for current collection and an LSM microelectrode generated from a patterned LSM electrode using an electrochemically etched tungsten-carbide tip, respectively. The height and width of the LSM patterned electrode and the space between two adjacent LSM electrodes are 0.8, 11.5, and 20 μm , respectively. The rest of the patterned LSM electrodes were used as the counter electrode (CE). By controlling the position of the LSM ME, we can separate the ME and CE by a single YSZ grain boundary, or put the ME and CE onto a single YSZ grain. Shown in Figure 2(c) is the effect of the LSM ME perimeter on LSM-YSZ interfacial impedance at 650°C. It was found that the Ohmic portion of the impedance decreased as the perimeter of the LSM ME was increased. In addition, we found that the product of the ME perimeter and the Ohmic portion of the impedance also decreased with an increase of the ME perimeter. The product should remain constant if triple-phase boundaries (TPBs) are single lines around the ME. It seems that the small ME has a larger perimeter specific resistance as compared to the larger perimeter MEs. A possible explanation is that some unobservable delamination caused by the scratching process has occurred. The smaller the ME, the higher the relative percentage of delaminated area and thus, the larger the Ohmic portion of the impedance resistance. The proposed delamination issue could be resolved by scratching the patterned ME before the annealing process. Specifically, after the patterned electrode was fabricated by the sputtering process, the ME would be scratched, and then annealed at higher temperature. Another observation was an

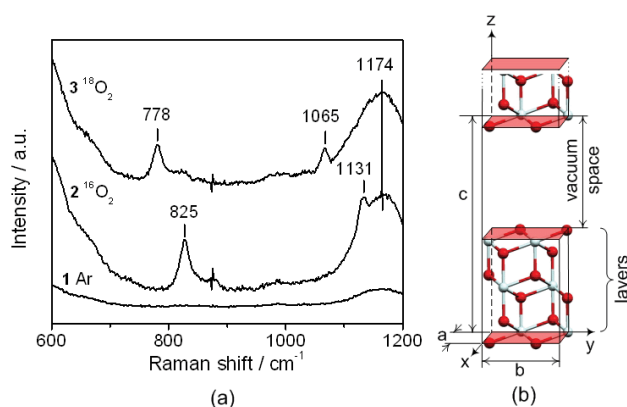


FIGURE 1. (a) A representative surface model with nine layers for the O_2 - CeO_2 (111) interactions. (b) Typical Raman spectra of CeO_2 sample treated by 5% H_2 at 673 K before 298 K exposure to (1) Ar, (2) 10% $^{16}O_2$, and (3) 10% $^{18}O_2$ atmospheres (all mixtures are diluted with Ar).

increase in the impedance with increased DC bias, suggesting the electrode reaction is mass transfer limited. Application of DC bias should not change the shape of the impedance spectrum, as the DC bias should only influence the non-ohmic component. After applying DC voltage, the impedance was collected without DC bias again. No significant change was found indicating that application of DC bias did not damage or alter the ME. More detailed studies to interpret the experimental observations with an electrochemical modeling are in progress.

We have developed a model to predict the electrochemical response of thin-film and patterned electrodes, which we then used to account for sheet resistance in 60 nm thick LSM thin films with current collectors 50 μm apart. We found that electrical potential increases along the length of the film between current collectors due to sheet resistance. Shown in Figure 3 is a simulated, normalized cathodic current density-voltage curve for the film. Note the Tafelian behavior in Figure 3. The semi-log scale in the left-hand plot of the figure reflects the shape of a co-limited process. In this case, the limiting factors are ionic

transport at low overpotentials, and sheet resistance at high overpotentials. The reason for the switch is that the vacancy transfer at the interface is potential-dependent, with an exponential response to potential changes (hence the Tafelian profile), while bulk electronic transport is only linearly responsive to potential. A greater concentration of vacancies in the bulk leads to higher ionic conductivity, in turn leading to greater sheet resistance losses. The problem is a difficult one to solve, since consideration of sheet resistance obviates the common assumption of ambipolar diffusion in MIECs, which simplifies the mathematics considerably but will not always be true for thin films. In addition, the problem is in two dimensions and is nonlinear. A numerical finite volume scheme was devised to solve the problem. The scheme used is time-dependent (even though the model results prior to steady-state are not reliable), which enables the use of a linear solver. This scheme works quite well at low overpotentials, however at cathodic overpotentials above 500 mV, the method slows down and ultimately becomes unstable. However, the instability in the numerical solver we have found so far is limited to high potential regions in which the material itself would not be chemically stable in reality.

As illustrated in Figure 4, oxygen permeation through dense silver membranes was determined to follow an Arrhenius relation with an activation energy of 0.94 eV (21.7 kcal mol⁻¹), which is comparable to literature values. The quantitative oxygen permeation and flux were also in agreement with reported values from the literature. Though oxygen permeation rates increased with temperature, the effective leaking current density generated at high temperatures (0.0146 mA cm⁻² at 750°C) is still minimal enough to allow silver to meet the gas separation requirements for SOFC materials.

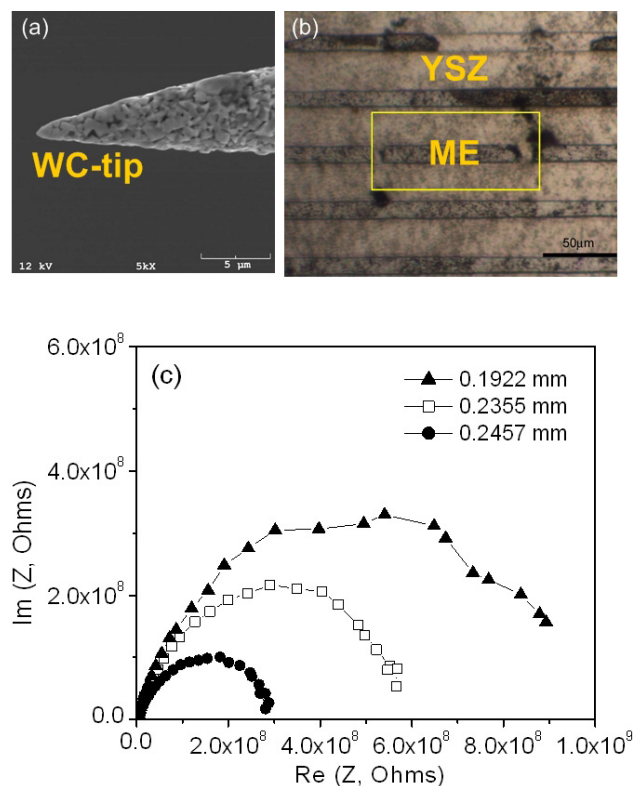


FIGURE 2. (a) An SEM image of a WC tip used for current collection of ME. (b) An LSM microelectrode generated from a patterned LSM electrode fabricated onto YSZ with large grains. (c) Impedance plots of the LSM microelectrode on YSZ at 650°C. The different plots correspond to the different ME perimeters listed in the plot. Note the decrease in overall impedance with increased the ME perimeter.

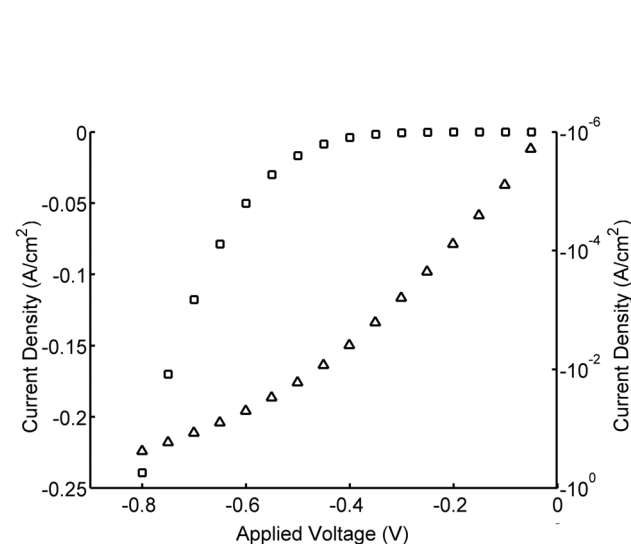


FIGURE 3. Current density-voltage curve for a 60 nm thick LSM film with current collectors 50 μm apart. Both linear (\square) and semilog (Δ) plots are shown.

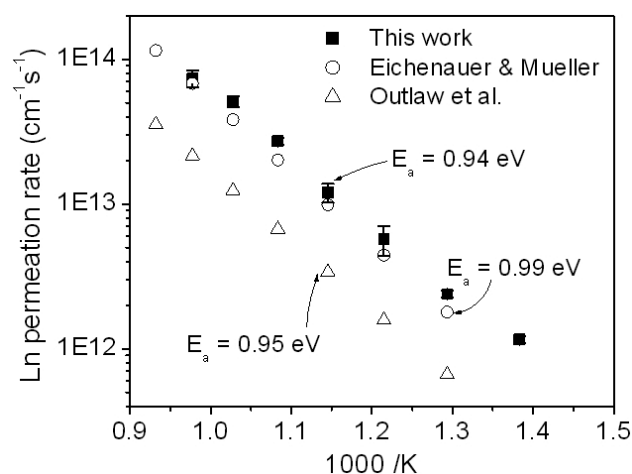


FIGURE 4. Arrhenius plot of measured oxygen permeation rate through dense silver versus inverse temperature (solid symbols) compared to literature values (open symbols).

Similar to what has been found in previous literature, degradation of the silver surface was observed to occur at the grain boundaries after only a few hours. A silver layer of about 12 μm (deposited by DC sputtering) was sufficient to prevent a quantifiable oxidation front within the Ni-YSZ anode after 8-hour exposure to SOFC operating conditions, nevertheless significant surface porosity was still observed. As silver theoretically makes a viable SOFC interconnect material for intermediate- and low-temperature SOFCs, the study on the grain boundary degradation will be examined in more detail for successful application.

Conclusions and Future Directions

In the past year, we made important progress in elucidation of the reaction mechanism of oxygen reduction on cathode materials for SOFCs by means of experimental and computational approaches. The combination of *in situ* Raman microscopy with *ab initio* calculations has provided detailed molecular-level information about surface adsorbed oxygen species. A model for electrochemical response was established to account for the effect of sheet resistance in LSM thin films using a numeric finite volume scheme. Silver was evaluated as a potential intermediate-temperature SOFC interconnect by measuring the oxygen permeation rate through dense silver membranes, which were determined to follow an Arrhenius relation with an activation energy of 0.94 eV (21.7 kcal mol⁻¹). Future studies are briefly outlined as follows.

- Suitable methods for application of noble metal nano-particles onto cathode materials, which result in acceptable surface enhanced Raman signals, need

to be developed. Once a method has been found that can generate a strong surface signal, we will use the mapping feature of our Raman spectrometer to explore the presence of this signal near and around the TPBs of our micropatterned electrode samples. In addition, advanced *ab initio* modeling will be carried out to interpret the surface adsorbed species detected by SERS.

- TPD and sticking probabilities for O₂-MIEC interactions will be conducted to identify surface adsorbed oxygen species and their desorption rates including the kinetics of adsorption and desorption.
- We plan to devise a steady-state scheme (not time-dependent) to model the DC response of MIEC thin films, which will require a nonlinear solver but should be much faster at high overpotentials. After combining the model with DFT calculations, it will be compared with experiments.

FY 2006 Publications/Presentations

Publications

- H. Chen, Y. Chen, A. Aleksandrov, J. Dong, M. Liu, and T. M. Orlando, "Charging Effects on Electron-Stimulated Desorption of Cations from Gadolinia-doped Ceria Surfaces", *Applied Surface Science*, 243(1-4), 166-177, 2005.
- H. Chen, A. Aleksandrov, Y. Chen, S. Zha, M. Liu, and T. M. Orlando, "Probing Water Interactions and Vacancy Production of Gadolinia-doped Ceria Surfaces Using Electron Stimulated Desorption", *Journal of Physical Chemistry B* 109 (22), 11257-11262, 2005.
- Y. Liu, E. Koep, and M. Liu, "A Highly Sensitive and Fast Responding SnO₂ Sensor Fabricated by Combustion Chemical Vapor Deposition (CVD)", *Chem. Mater.*, 17, 3997-4000, 2005.
- Y. Liu, M. Liu, "Creation of Porous Ceria by Sublimation of Tin Dioxide during Sintering", *Advanced Eng. Materials*, 8, 89-93, 2006.
- H. Chen, A. Aleksandrov, S. Zha, M. Liu, and T. M. Orlando, "Highly Efficient Electron Stimulated Desorption of O+ from Gadolinia-Doped Ceria Surfaces", *Journal of Physical Chemistry*, 110(22), 10779-10784, 2006.
- Y. Liu, M. Liu, "Porous SOFC Anodes Prepared by Sublimation of an Immiscible Metal Oxide during Sintering", *Electrochemical and Solid-State Letters*, 9(5), B25-B27, 2006.
- J. H. Wang, M. Liu and M.C. Lin, "Oxygen Reduction Mechanism on Ag/CeO₂ Cathodes of SOFCs", *Solid State Ionics*, 177(9-10), 939-947, 2006.
- D. Mebane and M. Liu, "Classical, phenomenological analysis of the kinetics of reactions at the gas-exposed surface of mixed ionic electronic conductors", *J. Solid State Electrochemistry*, 10(8), 575-580, 2006.

9. E. Koep, D. Mebane, R. Das, C. Compson, and M. Liu, "The Characteristic Thickness for a Dense LSM Electrode" *Electrochemical and Solid State Letters*, in press.
10. E. Koep, M. Liu, "Fabrication and Characterization of Thin-Film Mixed-Conducting Electrodes for Fundamental Studies", *Journal of Power Sources*, accepted.
11. R. Das, D. Mebane, E. Koep, and M. Liu, "Modeling of Patterned Mixed-Conducting Electrodes and the importance of sheet resistance at small feature sizes," *Solid State Ionics*, submitted.
12. H. T. Chen, Y. M. Choi, M. Liu, and M. C. Lin, "A Mechanistic Study of the Reduction of Ceria (111), (110) and (100) Surfaces by H₂", *J. Phys. Chem. B*, submitted.
13. Y. M. Choi, A. Harry, H. T. Chen, M. C. Lin, and M. Liu, "Characterization of O₂-CeO₂ interactions using in-situ Raman spectroscopy and first-principles calculations," *ChemPhysChem*, accepted.
14. H. Chen, A. Aleksandrov, Y. Chen, S. Zha, M. Liu, and T. M. Orlando, "Defect Structure of Gadolinia-doped Ceria Surfaces Using Electron Stimulated Desorption", *Journal of Physical Chemistry*, submitted.
15. D. Mebane and M. Liu, "Modeling of MIEC Cathodes: Effect of Sheet Resistance", *Ceramic Transitions*, in press.
16. Y. M. Choi, D. Mebane, M. C. Lin, and M. Liu, "Characterization of Oxygen Reduction on Electrochemically Active Cathode Surfaces in Solid Oxide Fuel Cells," *J. Alloys. Comp.*, to be submitted.
4. R. Das and M. Liu, "Modeling of Micro-Impedance Measurements of Mixed-Conducting Electrodes for SOFCs", Symposium for the Georgia Tech Strategic Energy Initiative, Atlanta, GA (2006).
5. J. Dong, R. Williams Jr., H. Abernathy, and M. Liu, "Characterization of Chromium Poisoning of SOFC's Cathodes", Symposium for the Georgia Tech Strategic Energy Initiative, Atlanta, GA (2006).
6. H. T. Chen, Y. M. Choi, M. Liu, and M. C. Lin, "A Theoretical Study of the Reduction of Ceria (111), (110) and (100) Surfaces by H₂", Vietnam-Taiwan Quantum Chemistry Conference, Taiwan (2005).
7. H. T. Chen, Y. M. Choi, M. Liu, and M. C. Lin, "A Computational Study of the Reduction of Ceria (111), (110) and (100) Surfaces by H₂", Chemical and Physical Processes in Combustion, FL (2005).
8. Y. M. Choi, M. C. Li, and M. Liu, "A Computational Study of Gas-Solid Interactions in Solid Oxide Fuel Cells", Georgia Local Section of the Electrochemical Society, Atlanta, GA (2005).
9. J. Dong, R. Williams Jr., and M. Liu, "Investigation of Reaction Mechanism of Ag/Gd Doped Ceria (GDC) Using Micro-Impedance Spectroscopy", Georgia Local Section of the Electrochemical Society, Atlanta, GA (2005).
10. D. Mebane and M. Liu, "Phenomenological Kinetics of Gas-Surface Reactions at Mixed Conducting Electrodes", Georgia Local Section of the Electrochemical Society, Atlanta, GA (2005).

Presentations

1. D. Mebane and M. Liu, "Modeling of MIEC Cathodes: Effect of Sheet Resistance", 30th International Conference & Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL. (2006).
2. H. Abernathy, Y. M. Choi, M. C. Lin, and M. Liu, "Characterization of Oxygen Reduction in Solid Oxide Fuel Cells", Symposium for the Georgia Tech Strategic Energy Initiative, Atlanta, GA (2006).
3. J. H. Wang and M. Liu, "Mechanism of Oxygen Reduction on a Ag/CeO₂ Based SOFC Cathode", Symposium for the Georgia Tech Strategic Energy Initiative, Atlanta, GA (2006).

References

1. S. Pizzini, Fast Ion Transport in Solids. (1973).
2. B. C. H. Steele, Solid State Ionics 86-88, 1223 (1996).
3. E. I. Tiffee and A. V. Virkar, High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications (Elsevier, New York, 2003).
4. R. Radhakrishnan, A. V. Virkar, and S. C. Singhal, J. Electrochem. Soc. 152 (5), A927 (2005).
5. Y. M. Choi, H. Abernathy, H. T. Chen, M. C. Lin, and M. Liu, ChemPhysChem, accepted (2006).